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Synthesis of bifunctional tetrakis(trimethylsilyl)silane derivatives

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Bifunctional derivatives $(XMe_2Si)_2Si(SiMe_3)_2$ (X = H, Cl, or OH) were synthesized for the first time by the reaction of tetrakis(trimethylsilyl)silane with $SbCl_5$. The molecular and crystal structure of bis(hydroxydimethylsilyl)bis(trimethylsilyl)silane was established by X-ray diffraction. The fragmentation of the resulting compounds under electron impact was studied by mass spectrometry.

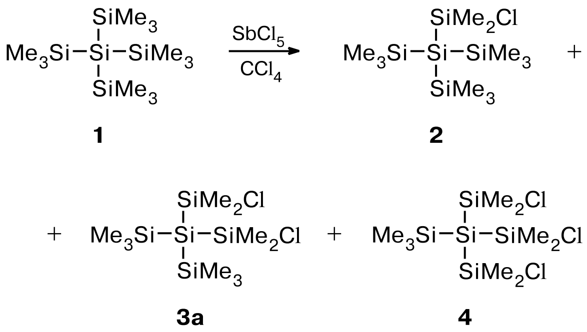
Key words: tetrakis(trimethylsilyl)silane, antimony pentachloride, bifunctional tetrakis(trimethylsilyl)silane derivatives, X-ray diffraction study, mass spectrometry.

Earlier, $SbCl_5$ has been used as a chlorodemethylating agent in the synthesis of dichloro derivatives of linear,[1,2] cyclic,[3—8] and bicyclic[9,10] permethylated silanes. In continuation of these studies and our research on the synthesis[11—13] of dichloro derivatives of permethyloligosilanes, which serve as synthons in the synthesis of polymers containing oligosilane fragments in the main chain by different macromolecular design, we examined the reaction of $SbCl_5$ with yet another representative of permethyloligosilanes, *viz.*, branched tetrakis(trimethylsilyl)silane $(Me_3Si)_4Si$ (**1**), and investigated the characteristic features of fragmentation of bifunctional derivatives of silane **1** under electron impact ionization (EI). It was also of interest to study the molecular and crystal structure of bis(hydroxydimethylsilyl)bis(trimethylsilyl)silane and estimate the energy parameters of the hydrogen bonds between the molecules in the crystalline state.

Results and Discussion

The reaction of silane **1** with $SbCl_5$ was performed at ~20 °C in CCl_4, which is the solvent of choice for chlorodemethylation[7] with $SbCl_5$ (Scheme 1). The GLC analysis demonstrated that the composition of the reaction mixture* substantially depends on the ratio of the starting reagents (Table 1). For example, only (chlorodimethylsilyl)tris(trimethylsilyl)silane (**2**) is generated if the silane **1** : $SbCl_5$ ratio is in the range from 1 : 0.2 to 1 : 1, the conversion of the starting silane **1** being insufficiently high. At **1** : $SbCl_5$ = (1 : 1.2)—(1 : 1.8), the conversion of silane **1** is 100%, the percentage of bis(chlorodimethylsilyl)bis(trimethylsilyl)silane (**3a**) in the reaction products being substantially increased with increasing amount of antimony pentachloride. The maximum yield of silane **3a** is observed when the reagents are used in a ratio of 1 : 1.8 (see Table 1).

Scheme 1



The reaction performed with the use of the silane **1** to $SbCl_5$ ratio of 1 : 2 afforded, among other products, tris(chlorodimethylsilyl)(trimethylsilyl)silane (**4**) in trace amounts, whereas the percentage of silane **4** increased to 84% when **1** : $SbCl_5$ = 1 : 3.2 (see Table 1).

Attempts to separate chlorine-containing silanes **2** and **3a** by fractionation of their mixture failed. Bis(hydroxydimethylsilyl)bis(trimethylsilyl)silane (**3b**) was isolated by fractional crystallization of the hydrolysis products of a mixture of silanes **2** and **3a**. The reaction of compound **3b** with acetyl chloride gave dichlorine-containing silane **3a** in 96% yield (Scheme 2). An analogous procedure based on hydrolysis followed by treatment of the reaction products with acetyl chloride has been used earlier[10] for sepa-

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* The reaction products were identified based on empirical mass spectrum—structure relationships.

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Table 1. Dependence of the composition of the reaction mixture in the reaction of silane **1** with $SbCl_5$ on the reagent ratio

Run	**1** : $SbCl_5$	Composition of the reaction mixture^a (%)		
		1	**2**	**3a**
1	1 : 0.2	87	13	—
2	1 : 0.4	63	37	—
3	1 : 0.6	44	56	—
4	1 : 0.8	38	62	—
5	1 : 1.0	26	63	11
6	1 : 1.2	9	67	24
7	1 : 1.4	—	60	40
8	1 : 1.6	—	47	53
9	1 : 1.8	—	24	76
10	1 : 2.0	—	20	80^b
11	1 : 3.2	—	—	16^c

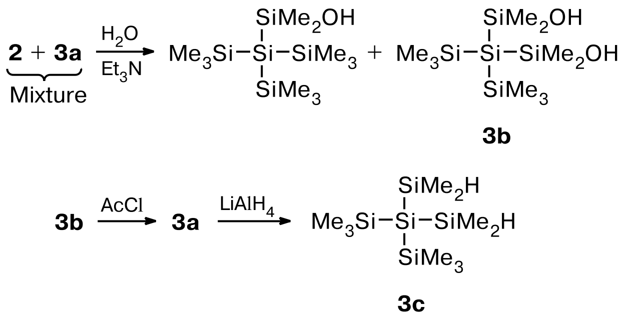
[a] GLC data.

[b] The reaction mixture contains traces of silane **4** (<0.1%).

[c] The reaction mixture contains 84% of silane **4**.

ration of the structural isomers of dichlorodecamethylcyclohexasilane. Bis(hydrodimethylsilyl)bis(trimethylsilyl)silane (**3c**) was synthesized in 85% yield by the reaction of silane **3a** with $LiAlH_4$.

Scheme 2



$$\underbrace{\mathbf{2}+\mathbf{3a}}_{\text{Mixture}} \xrightarrow[Et_3N]{H_2O} Me_3Si\text{-}\overset{SiMe_2OH}{\underset{SiMe_3}{Si}}\text{-}SiMe_3 + Me_3Si\text{-}\overset{SiMe_2OH}{\underset{SiMe_3}{Si}}\text{-}SiMe_2OH$$

3b

$$\mathbf{3b} \xrightarrow{AcCl} \mathbf{3a} \xrightarrow{LiAlH_4} Me_3Si\text{-}\overset{SiMe_2H}{\underset{SiMe_3}{Si}}\text{-}SiMe_2H$$

3c

The molecular and crystal structure of silane **3b** was established by X-ray diffraction. Two independent molecules in the crystal structure of **3b** differ in the arrangement of the hydroxy groups with respect to the Si(2)Si(3)Si(4) plane (Fig. 1, Table 2). In one independent molecule, both OH groups are on the same side of the Si(2)Si(3)Si(4) plane (the angles between the Si(2)—O(1) and Si(3)—O(2) bonds and this plane (Δ_1 and Δ_2, respectively) are 29.3(2) and 15.8(3)°). In another independent molecule, the OH groups are on the opposite sides of the Si(2′)Si(3′)Si(4′) plane (the Δ'_1 and Δ'_2 angles are 85.2(3) and 164.3(3)°, respectively). The Si—O, Si—Si, and Si—C bond lengths are typical of this class of compounds.[14]

The differences in the configuration of two independent molecules in the crystal structure of silane **3b** are, apparently, due to rotation about the Si—Si and Si—O bonds. To study the conformational behavior of molecule **3b** and its dependence on the crystal packing, we performed quantum chemical calculations for both the crystal and isolated molecule **3b** with the use of the CPMD program and a plane wave basis set. An analysis of the calculated bond lengths in the crystal and the conformers of isolated molecule **3b** (see below) demonstrated that the Si—O and Si—Si bond lengths are always systematically elongated by 0.02—0.03 Å compared to the experimental values. Such differences are typical of calculations by density functional theory.[15] The Si—C bond lengths and the bond angles were reproduced within 0.01 Å and 3°, respectively.

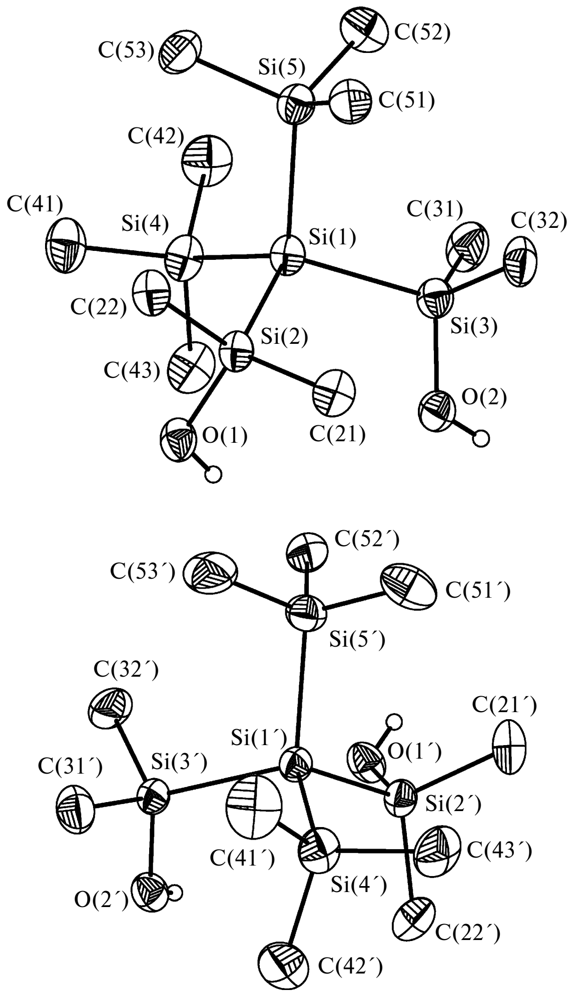


Fig. 1. Molecular structures of two independent molecules in the crystal of **3b** represented by anisotropic displacement ellipsoids at the 50% probability level.

An analysis of the potential energy surface of isolated molecule **3b** revealed three conformers (**A**, **B**, and **C**), which differ in the arrangement of the hydroxy groups with respect to the Si(2)Si(3)Si(4) plane (Fig. 2, Table 3). The relative arrangement of the OH groups in con-

Table 2. Experimental and calculated (CPMD program) geometric parameters of silane **3b**

Parameter	Experiment	Calculation
Bond	*d*/Å	
Si(1)—Si(2)	2.356(1)	2.374
Si(1)—Si(3)	2.337(2)	2.354
Si(1)—Si(4)	2.354(1)	2.374
Si(1)—Si(5)	2.355(2)	2.370
Si(2)—O(1)	1.663(2)	1.689
Si(3)—O(2)	1.657(3)	1.692
Si(1´)—Si(2´)	2.340(1)	2.364
Si(1´)—Si(3´)	2.349(1)	2.371
Si(1´)—Si(4´)	2.346(2)	2.364
Si(1´)—Si(5´)	2.341(1)	2.358
Si(2´)—O(1´)	1.659(2)	1.692
Si(3´)—O(2´)	1.670(3)	1.693
Angle	φ/deg	
Δ_1	28.9(3)	28.6
Δ_2	15.8(2)	16.3
Δ'_1	85.2(3)	85.1
Δ'_2	164.4(3)	164.1
Si(1)—Si(2)—O(1)—H(1)	66	115
Si(1)—Si(3)—O(2)—H(2)	166	71
Si(1´)—Si(2´)—O(1´)—H(1´)	62	107
Si(1´)—Si(3´)—O(2´)—H(2´)	158	70

Note. Δ_1 and Δ_2 and the angles between the Si(2)Si(3)Si(4) plane and the Si(2)—O(1) and Si(3)—O(2) bonds, respectively; Δ'_1 and Δ'_2 the analogous parameters for the second independent molecule.

formers **A**, **B**, and **C** can be described by the Si(1)—Si(2)—O(1)—H(1) and Si(1)—Si(3)—O(2)—H(2) torsion angles (see Table 3). The arrangement of the hydroxy groups in conformers **A** and **C** is similar to that in two independent molecules in the crystal of **3b** (see Tables 2 and 3). Conformer **A** is characterized by the presence of the weak intramolecular O(1)—H(1)...O(2) bond (the O(1)...O(2) and O(2)...H(1) distances are 2.91 and 1.98 Å, respectively; the O(1)—H(1)...O(2) angle is 156°). The even weaker O(1)—H(1)...O(2) bond was found in conformer **C** (the O(1)...O(2) and O(2)...H(1) distances are 3.00 and 2.10 Å, respectively; the O(1)—H(1)...O(2) angle is 152°). In conformer **B**, the hydrogen bond is absent and the mutual arrangement

Table 3. Geometric parameters of conformers **A**—**C** of isolated molecule **3b**

Parameter	A	B	C
Bond		*d*/Å	
Si(1)—Si(2)	2.384	2.376	2.390
Si(1)—Si(3)	2.367	2.362	2.376
Si(1)—Si(4)	2.378	2.374	2.375
Si(1)—Si(5)	2.373	2.375	2.377
Si(2)—O(1)	1.676	1.689	1.679
Si(3)—O(2)	1.707	1.691	1.707
H(1)...O(2)	1.983	—	2.102
Angle		φ/deg	
O(1)—H(1)...O(2)	156	—	152
Si(1)—Si(2)—O(1)—H(1)	43	53	69
Si(1)—Si(3)—O(2)—H(2)	179	177	50

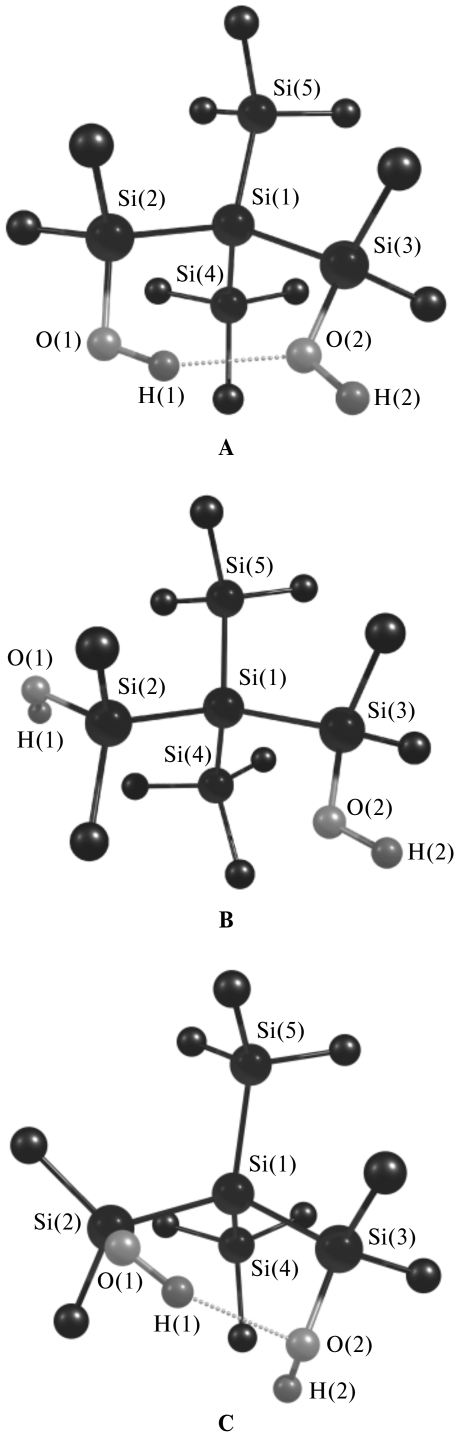


Fig. 2. Molecular structures of conformers **A**, **B**, and **C** of isolated molecule **3b**.

of the hydroxy groups can be described as antiperiplanar (the O(1)—Si(2)—Si(3)—O(2) pseudotorsion angle is 156°).

The total energies of conformers **A** and **C** are lower than that of conformer **B** by 2.67 and 1.66 kcal mol^{-1}, respectively. Apparently, the observed difference is attributed to the formation of the weak intermolecular O(1)—H(1)...O(2) bond. Therefore, the structure of isolated molecule **3b** is more likely to correspond to conformer **A** or **C**. In the crystal of **3b**, intramolecular hydrogen bonding is absent; instead, two independent molecules are linked to each other *via* "cooperative" intermolecular hydrogen bonds to form chains (Fig. 3). The intermolecular contacts between the Me groups correspond to weak van der Waals interactions. The three-dimensional crystal structure was reproduced by quantum chemical calculations with good accuracy. The differences between the experimental and calculated interatomic distances corresponding to intermolecular contacts are ~0.1 Å. The O—H...O bond parameters were reproduced with higher accuracy (see Fig. 3). Analysis of the published data[16] demonstrated that generalized gradient approximation functionals underestimate the energy of weak intermolecular interactions. The interaction energy of molecule **3b** with its crystal environment (E_{in}) can be evaluated as the difference between the crystal energy (calculated by the quantum chemical method) and the energies of conformers **A** and **B** taking into account the number of the formula units, almost only hydrogen bonds making a contribution to this value. The calculated energies E_{in} are 5.62 and 8.33 kcal mol^{-1}, respectively. The formation of two hydrogen bonds in conformer **A** leads to an energy gain of 5.62 kcal mol^{-1} and the disappearance of the intramolecular O(1)—H(1)...O(2) bond. In the crystal, each molecule **3b** forms two hydrogen bonds. Hence, the average strength of each hydrogen bond can be estimated as one-half of E_{in} (4.17 kcal mol^{-1}), which falls in the range for the hydrogen bonds in silanols.[17]

These data can be used for the description of the characteristic features of aggregation of molecules **3b** and analogous molecules in solution and mesophases, whose structures cannot be studied with the same accuracy as in crystals.

The fragmentation of silane **1** and its bifunctional derivatives **3a—c** was studied by mass spectrometry with electron impact ionization.

The mass-spectrometric data on branched silanes are limited primarily to the spectra of 2,2-bis(silyl)trisilane[18] and substituted tris(trimethylsilyl)silanes[19] $(Me_3Si)_3SiX$ (**5**) (X = H, Cl, or $Si(SiMe_3)_3$). The spectrum of silane **1**, like the spectrum of silane **5** with X = $Si(SiMe_3)_3$, has the intense molecular ion peak $[M]^+$ (Table 4). It should be noted that the peak $[M]^+$ is absent in the spectrum of tetrakis(trimethylsilyl)methane (the carbon analog of silane **1**).[20] The spectra of bifunctional derivatives **3a—c** contain a weak, if any, peak $[M]^+$ (see Table 4). An analogous decrease in the intensity of the peak $[M]^+$ has been observed earlier[19] in the spectra of branched silanes **5** in going from X = H to X = Cl.

The main fragmentation pathways of the $[M]^+$ ion of silane **1** and its derivatives **3a—c** involve elimination of Me radicals and Si—Si bond cleavage. As an example, the

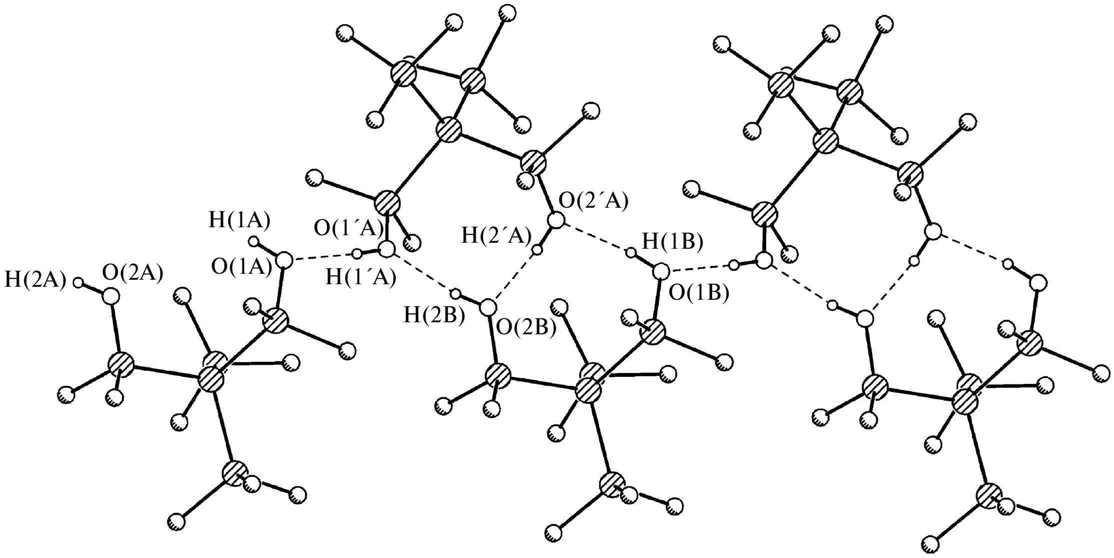


Fig. 3. Chains in the crystal packing of **3b** formed *via* weak O—H...O bonds. The experimental [calculated] parameters of the O—H...O bonds (O...O and H...O interatomic distances (Å) and O—H...O angles (deg), respectively): O(1B)—H(1B)...O(2´A) (*x*, *y* – 1, *z*), 2.781(4) [2.746], 1.94, and 172 [167]; O(2B)—H(2B)...O(1´A) (*x*, *y* – 1, *z*), 2.782(4) [2.782], 1.96, and 162 [165]; O(2´A)—H(2´A)...O(2B) (*x*, *y* + 1, *z*), 2.731(4) [2.715], 1.90, and 168 [171]; O(1´A)—H(1´A)...O(1A), 2.793(4) [2.775], 1.95, and 174 [174].

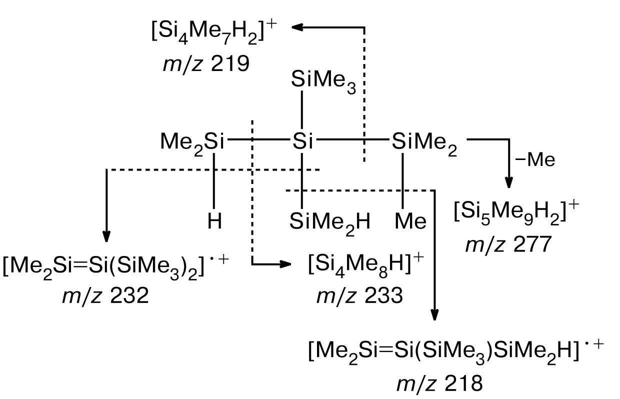
Table 4. Mass spectra of silane **1** and its derivatives **3a—c***

Ion	m/z (I_{rel} (%))			
	1	**3a**	**3b**	**3c**
$[M]^+$	320 (61.9)	—	—	292 (3.4)
$[M - Me]^+$	305 (35.7)	345 (3.7)	309 (1.8)	277 (5.1)
$[M - SiMe_3]^+$	247 (5.1)	—	251 (1.7)	219 (1.3)
$[M - SiMe_2X]^+$	—	267 (3.1)	249 (3.3)	233 (4.2)
$[M - SiMe_4]^+$	232 (100)	—	—	—
$[M - SiMe_3X]^{\bullet +}$	—	252 (52.1)	234 (33.8)	218 (100)
$[M - SiMe_2X_2]^{\bullet +}$	—	232 (10.7)	232 (37.1)	232 (21.6)
$[Me_3Si]^+$	73 (54.4)	73 (100)	73 (100)	73 (83.6)
$[Me_2SiX]^+$	—	93 (13.4)	75 (42.3)	59 (17.5)

* X = Cl (**3a**), OH (**3b**), or H (**3c**).

fragmentation of the $[M]^+$ ion of silane **3c** is shown in Scheme 3.

Scheme 3



The intensity of the ion peak $[M - Me]^+$ in the mass spectrum of silane **1** (like that in the spectra of branched silanes **5**) is much lower compared to simple silanes,[21] the introduction of functional substituents into molecule **1** resulting in a substantial decrease in the intensity of this peak (see Table 4). By contrast, the peak $[M - Me]^+$ in the spectrum of tetrakis(trimethylsilyl)methane has the maximum intensity.[20]

Compared to the linear permethyloligosilanes[22—25] $X(Me_2Si)_nX$ (X = Me, Cl, or All), the Si—Si bond cleavage processes accompanied by the charge localization on the central silicon atom in silanes **1** and **3a—c** are less pronounced. The mass spectra contain weak (≤5%), if any, ion peaks $[M - SiMe_3]^+$ and $[M - SiMe_2X]^+$, which is characteristic also of branched silanes **5**. For example, the intensity of the peak $[M - SiMe_3]^+$ for silane **5** with $X = Si(SiMe_3)_3$ is 7.9%, whereas this peak is absent at all in the mass spectra of silanes with X = H or Cl. In the case of branched silanes, this process is less pronounced due to an efficient competitive stabilization of the positive charge on the leaving substituents. For example, the highest peaks in the spectra of silanes **1** and **3a—c** correspond to the $[SiMe_3]^+$ and $[SiMe_2X]^+$ ions or, at least, these peaks are characterized by high intensity (see Table 4). This is also true for branched silanes **5**.[20] The intensities of the peaks of the corresponding ions are 20—100%.

The characteristic and dominating decomposition process of silanes **1** and **3a—c** is associated with the formation of the disilylene radical cations $[Me_2Si{=}Si(SiMe_3)SiMe_2X]^{\bullet +}$ and $[Me_2Si{=}Si(SiMe_3)_2]^{\bullet +}$ (see Scheme 3). The formation of odd-electron disilylene radical cations is a common feature of the mass spectra of both linear permethyloligosilanes[22—25] and substituted tris(trimethylsilyl)silanes.[19] Presumably, the disilylene ions are generated from the molecular ion upon elimination of the neutral Me_3SiX and Me_2SiX_2 species through a four-membered transition state. In the case of permethyloligosilanes,[24] the formation of disilylenes directly from the molecular ion was confirmed by investigation of metastable transitions and high-resolution mass spectra.

To summarize, we synthesized the previously unknown bifunctional tetrakis(trimethylsilyl)silane derivatives and studied their chemical properties.

Experimental

The ^{29}Si NMR spectra were recorded on a Bruker WP-400 SY spectrometer with Me_4Si as the internal standard. The GLC analysis was carried out on an LKhM-8MD chromatograph (0.3×100-cm stainless steel column, 5% SE-30 on Chromaton N-AW-DMCS, a thermal conductivity detector, temperature programming from 30 to 300 °C at a rate of 12 °C min^{-1}, helium as the carrier gas). The mass spectrometric analysis was carried out on an HP-5890 instrument (20 m × 0.32-mm capillary column, SE-30 liquid phase, helium as the carrier gas, the temperature of the injector and transition lines was 250 °C, ionizing voltage was 70 eV, temperature programming from 60 to 300 °C at a rate of 7 K min^{-1}).

Tetrakis(trimethylsilyl)silane (**1**) was synthesized according to a procedure described earlier[26] (the yield was 55%). Diethyl ether was dried by refluxing followed by distillation under a stream of argon over metallic sodium in the presence of benzophenone. Carbon tetrachloride and petroleum ether were dried by distillation under argon over P_2O_5. Hexane, acetyl chloride, and acetonitrile were distilled under a stream of argon immediately before use. Triethylamine was distilled under argon over NaOH granules. The reagents $SbCl_5$ (Merk) and $LiAlH_4$ (Aldrich) were used without additional purification. The reactions of silane **1** with $SbCl_5$ and the synthesis of silanes **3a,c** were carried out under dry argon.

Reaction of tetrakis(trimethylsilyl)silane (1) with $SbCl_5$ (see Table 1, run *9*). A solution of $SbCl_5$ (5.27 g, 17.6 mmol) in CCl_4 (5 mL) was added dropwise with vigorous stirring to a solution of silane **1** (3.0 g, 9.4 mmol) in CCl_4 (35 mL). The reaction mixture was stirred for 12 h. The precipitate of Me_2SbCl_3 was filtered off, the solvent was removed *in vacuo*, the residue was extracted with petroleum ether (2×3 mL), and the extract was washed with a small amount of acetonitrile to remove antimony compounds. The solvent was removed *in vacuo* and the reaction product, which contained (GLC data) silanes **2** (26%) and **3a** (74%), was obtained in a yield of 3.2 g.

Runs *1—8*, *10*, and *11* were carried out analogously (see Table 1).

Bis(hydroxytrimethylsilyl)bis(trimethylsilyl)silane (3b). A solution of a mixture of silanes **2** and **3a** (3.2 g, 8.6 mmol) in hexane (15 mL) was added to a mixture of distilled water (8 mL), Et_3N (1.9 g, 18.8 mmol), and hexane (25 mL) with vigorous stirring. The reaction mixture was stirred for 1 h, the organic layer was separated, and the solvent was removed *in vacuo*. The crystalline precipitate was twice recrystallized from hexane (2×2 mL). Silane **3b** was obtained in a yield of 1.4 g (63.9% based on consumed silane **3a**). Found (%): C, 36.76; H, 9.88; Si, 43.11. $C_{10}H_{32}O_2Si_5$. Calculated (%): C, 36.98; H, 9.93; Si, 43.24. ^{29}Si NMR (acetone-d_6), δ: 24.14 ($SiMe_2OH$); −5.68 ($SiMe_3$); −131.60 (Si).

Bis(chlorodimethylsilyl)bis(trimethylsilyl)silane (3a). Crystals of silane **3b** (1.4 g, 4.3 mmol) were suspended in acetyl chloride (5 mL). After a short period of time, an exothermic reaction started, and the crystals were dissolved. The solvent was removed *in vacuo* and silane **3a** was obtained in a yield of 1.5 g (96.2%). Found (%): C, 33.64; H, 8.38; Cl, 19.35; Si, 38.63. $C_{10}H_{30}Cl_2Si_5$. Calculated (%): C, 33.21; H, 8.36; Cl, 19.60; Si, 38.83. ^{29}Si NMR ($CDCl_3$), δ: 30.86 ($SiMe_2Cl$); −9.70 ($SiMe_3$); −123.57 (Si).

Bis(hydrodimethylsilyl)bis(trimethylsilyl)silane (3c). A suspension of $LiAlH_4$ (0.19 g, 5 mmol) in anhydrous diethyl ether (2 mL) was slowly added dropwise to a solution of silane **3a** (0.9 g, 2.5 mmol) in anhydrous diethyl ether (5 mL) at 0—5 °C. The reaction mixture was warmed to ~20 °C and stirred for 30 min. Then a mixture of ice (5 g) and concentrated HCl (0.5 mL) was added to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with petroleum ether (3×2 mL). The combined organic phases were dried with Na_2SO_4. The solvents were removed *in vacuo* at ~20 °C and silane **3c** was obtained in a yield of 0.62 g (85.1%) as a partially crystalline compound. Found (%): C, 41.34; H, 10.96; Si, 47.70. $C_{10}H_{32}Si_5$. Calculated (%): C, 41.02; H, 11.02; Si, 47.96. ^{29}Si NMR (C_6D_6), δ: −7.92 ($SiMe_3$); −17.42 ($SiMe_2H$); −127.68 (Si).

X-ray diffraction study of silane 3b. The crystals of $C_{10}H_{32}O_2Si_5$ are monoclinic, space group $P2_1/c$, a = 12.997(3) Å, b = 9.1862(19) Å, c = 35.053(8) Å, β = 98.632(5)°, V = 4137.7(16) Å^3, Z = 8, M = 324.81, d_{calc} = 1.043 g cm^{-3}, μ(Mo-Kα) = 0.338 mm^{-1}, F(000) = 1424. The intensities of 26180 reflections were measured on a Bruker Smart CCD 1000K diffractometer at 120 K (λ(Mo-Kα) = 0.71072 Å, ω-scanning technique, 2θ < 54°), and 9063 independent reflections (R_{int} = 0.0643) were used in the refinement. The structure of silane **3b** was solved by direct methods and refined by the full-matrix least-squares method against F^2 with anisotropic and isotropic displacement parameters. The hydrogen atoms of the Me groups were calculated geometrically and refined using a riding model with U(H) = 1.5U_{eq}(C). The hydrogen atoms of the OH groups were located from difference Fourier maps and normalized to the ideal O—H distances (0.85 Å) with a constant isotropic displacement parameter U_{eq} (0.05 Å^2). The final characteristics of the refinement were as follows: wR_2 = 0.1300 (using all reflections), GOF = 1.02, R_1 = 0.0598 (using 5223 reflections with $I > 2\sigma(I)$). All calculations were carried out with the use of the SHELXTL-97 program package (version 5.10)[27] on IBM PC.

Quantum chemical calculations. Quantum chemical calculations for the crystal of **3b** and isolated molecule **3b** were carried out with full geometry optimization by density functional theory (the PBE exchange-correlation functional) with the use of a plane wave basis set (the kinetic energy was lower than 25 Ry) and the CPMD 3.7.2 program.[28] Vanderbilt's pseudopotentials[17] were utilized to account for the component of the wavefunction corresponding to the core electrons.[29] The correspondence of isomers **A—C** to minima on the potential energy surface was proved by calculating the frequencies in the vibrational spectrum. The crystal structure of **3b** was optimized with the use of the experimental unit cell parameters, which were kept fixed, and the X-ray diffraction data were used as the starting atomic configuration. The calculations were carried out with consideration for only the Γ point in the Brillouin zone, which seemed to be sufficient for calculations of the total crystal energy taking into account the large unit cell volume. The frequencies in the vibrational spectrum of the crystal of **3b** were not calculated because such calculations require large computer resources.

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